

AD-A077 574

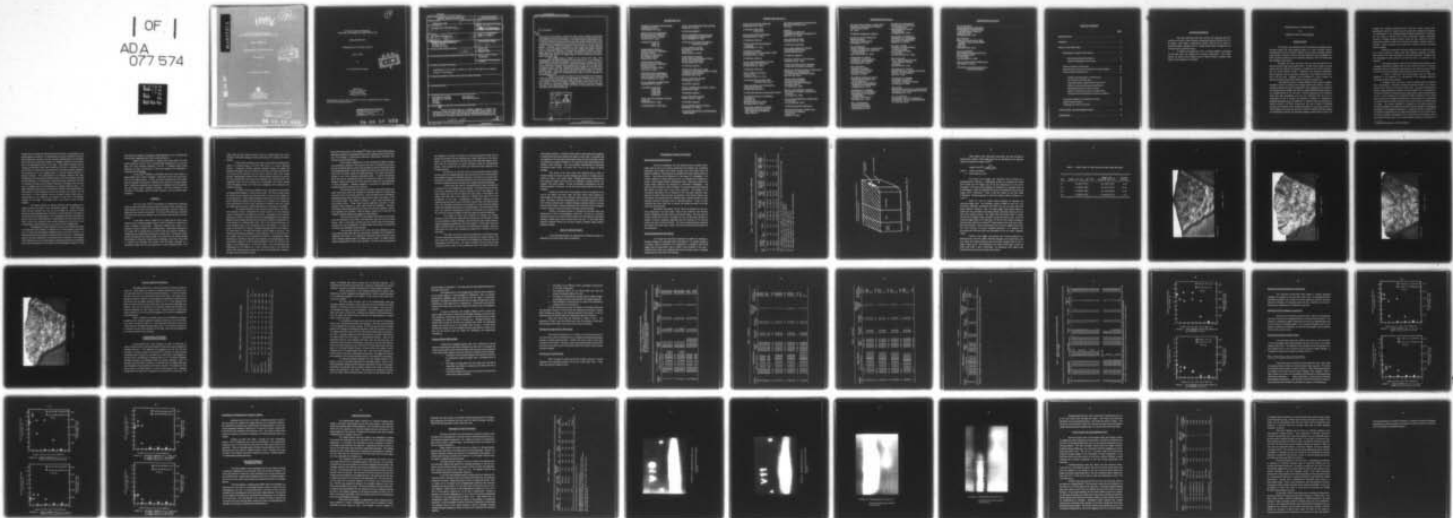
BATTELLE COLUMBUS LABS OH
HYDROGEN IN HY-130 WELD METAL.(U)
MAY 79 M D HAYES , D HAUSER

F/G 11/6

UNCLASSIFIED

N00014-74-C-0407
NL

| OF |
ADA
077 574



END
DATE
FILMED
1 - 80
DDC

12

OFFICE OF NAVAL RESEARCH
CONTRACT NO. N00014-74-C-0407 (NR 031-770)

FINAL REPORT ON

HYDROGEN IN HY-130 WELD METAL

May 14, 1979

by

M. D. Hayes and D. Hauser

DDC
RECEIVED
DEC 3 1978
E

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Reproduction of this report in whole or in part is permitted for any purpose of the United States government.

This document has been approved
for public release and sale; its
distribution is unlimited.

H

79 08 27 035

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER N00014-74-C-0407	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9	4. TYPE OF REPORT & PERIOD COVERED Final rept. July 1977 - December 1978
4. TITLE (and Subtitle) 6 Hydrogen in HY-130 Weld Metal	7. AUTHOR(s) 10 A. D. Hayes and X Hauser Michael Daniel	8. CONTRACT OR GRANT NUMBER(s) 15 N00014-74-C-0407	6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle-Columbus Laboratories 505 King Avenue Columbus OH 43201	11. CONTROLLING OFFICE NAME AND ADDRESS 12 55	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 11 14 May 79	12. REPORT DATE May 14, 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	13. NUMBER OF PAGES	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Reproduction of this report in whole or in part is permitted for any purpose of the U. S. Government.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Gas Metal Arc Welding Embrittlement Submerged Arc Welding Rare Earth Materials HY-130 Hydrogen			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This is the final report on a program designed to evaluate the potential for using rare-earth materials to getter hydrogen during welding. The end objective was to reduce the potential for hydrogen embrittlement in HY-130 steel welds. This report briefly summarizes work conducted during the first			

407 080

403
(Continued)

20. (Continued)

three years of the program, during which time several varieties of rare-earth containing-electrodes were produced. Cracking problems during drawing were encountered when rare-earth materials were added to high-strength filler wires. A method of addition was found wherein rare-earth silicon and rare-earth nickel compounds were incorporated into a rare-earth cored wire. This wire was then used as a cold-wire addition and weldments were produced by the gas metal-arc process. However, impact properties of these welds were below specified limits. This was partially attributed to the poor welding performance resulting from the rare-earth additions. Increased arc instability resulted in spatter, bead irregularity, and poor wetting action. Weldability improved when argon-O₂ mixtures were used but the oxygen addition to the shielding gas oxidized all of the rare earths.

Most of this report is dedicated to the fourth year's work. Both metallographic and button-melting tests were carried out in an attempt to understand why mechanical properties were lowered and to improve the rare-earth transfer from wire to weld pool. Microprobe analysis revealed that little, if any, rare-earth materials were transferred from filler wire to weld metal during gas metal-arc welding. Hydrogen-gettering experiments indicated that a rare-earth nickel-cored wire without iron powder additions was the strongest gettering agent. These tests also showed that after one melting of the rare earth with filler metals the hydrogen-gettering ability was lost, regardless of the shielding gas used.

Finally in an attempt to protect the rare-earth filler from oxidation, a cold-wire addition was made to the submerged-arc welding process. Success of this method was indicated when welds made with a wet flux and the rare-earth addition showed no hydrogen cracking; whereas, welds made with a wet flux without a rare-earth addition exhibited delayed transverse hydrogen cracking. These results suggest that rare earths in covered electrode coatings may help prevent hydrogen cracking.

Accession For	
NTIS	GRA&I
DDC	TAB
Unannounced	
Justification	<i>Per file</i>
By	<i>[Signature]</i>
Distribution/	
Availability Codes	
Dist	Avail and/or special
<i>A</i>	

DISTRIBUTION LIST

DEFENSE DOCUMENTATION CENTER
CAMERON STATION
ALEXANDRIA VA 22314

OFFICE OF NAVAL RESEARCH
DEPARTMENT OF THE NAVY
800 NORTH QUINCY STREET
ARLINGTON VA 22217

ATTENTION CODE 471
CODE 102
CODE 470

COMMANDING OFFICER
OFFICE OF NAVAL RESEARCH
BRANCH OFFICE
BUILDING 114, SECTION D
666 SUMMER STREET
BOSTON MA 02210

COMMANDING OFFICER
OFFICE OF NAVAL RESEARCH
BRANCH OFFICE
536 SOUTH CLARK STREET
CHICAGO IL 60605

OFFICE OF NAVAL RESEARCH
SAN FRANCISCO AREA OFFICE
ONE HALLIDIE PLAZA SUITE 601
SAN FRANCISCO CA 94102

NAVAL RESEARCH LABORATORY
WASHINGTON DC 20375

ATTENTION CODE 6000
CODE 6100
CODE 6300
CODE 6400
CODE 2627

NAVAL AIR DEVELOPMENT CENTER
CODE 302
WARMINSTER PA 18964

ATTENTION MR F S WILLIAMS

NAVAL AIR PROPULSION TEST CENTER
TRENTON NJ 08628

ATTENTION LIBRARY

NAVAL CONSTRUCTION BATTALION
CIVIL ENGINEERING LABORATORY
PORT HUENEME CA 93043

ATTENTION ELECTRON MATERIALS
SCIENCES DIVISION

NAVAL MISSILE CENTER
MATERIALS CONSULTANT
CODE 3312-1
POINT MUGU CA 92041

COMMANDING OFFICER
NAVAL SURFACE WEAPONS CENTER
WHITE OAK LABORATORY
SILVER SPRING MD 20910

ATTENTION LIBRARY

DAVID W TAYLOR NAVAL SHIP
RESEARCH AND DEVELOPMENT CENTER
MATERIALS DEPARTMENT
ANNAPOLIS MD 21402

NAVAL UNDERSEA CENTER
SAN DIEGO CA 92132

ATTENTION LIBRARY

NAVAL UNDERWATER SYSTEM CENTER
NEWPORT RI 02840

ATTENTION LIBRARY

NAVAL WEAPONS CENTER
CHINA LAKE CA 93555

ATTENTION LIBRARY

NAVAL POSTGRADUATE SCHOOL
MONTEREY CA 93940

ATTENTION MECHANICAL ENGINEERING
DEPARTMENT

DISTRIBUTION LIST (Cont.)

NAVAL AIR SYSTEMS COMMAND
WASHINGTON DC 20360

ATTENTION CODE 52031
CODE 52032

NAVAL SEA SYSTEM COMMAND
WASHINGTON DC 20362

ATTENTION CODE 035

NAVAL FACILITIES ENGINEERING
COMMAND
ALEXANDRIA VA 22331

SCIENTIFIC ADVISOR
COMMANDANT OF THE MARINE CORPS
WASHINGTON DC 20380

ATTENTION CODE AX

NAVAL SHIP ENGINEERING CENTER
DEPARTMENT OF THE NAVY
WASHINGTON DC 20360

ATTENTION CODE 6101

ARMY RESEARCH OFFICE
P O BOX 12211
TRIANGLE PARK NC 27709

ATTENTION METALLURGY AND
CERAMICS PROGRAM

ARMY MATERIALS AND MECHANICS
RESEARCH CENTER
WATERTOWN MA 02172

ATTENTION RESEARCH PROGRAMS OFFICE

AIR FORCE OFFICE OF SCIENTIFIC
RESEARCH
BUILDING 410
BOLLING AIR FORCE BASE
WASHINGTON DC 20332

ATTENTION CHEMICAL SCIENCE
DIRECTORATE, ELECTRONICS
AND SOLID STATE SCIENCES
DIRECTORATE

AIR FORCE MATERIALS LABORATORY
WRIGHT-PATTERSON AFB
OH 45433

LIBRARY
BUILDING 50, ROOM 134
LAWRENCE RADIATION LABORATORY
BERKELEY CA 94704

NASA HEADQUARTERS
WASHINGTON DC 20546

ATTENTION CODE RRM

NASA LEWIS RESEARCH CENTER
21000 BROOKPARK ROAD
CLEVELAND OH 44135

ATTENTION LIBRARY

NATIONAL BUREAU OF STANDARDS
WASHINGTON DC 20234

ATTENTION METALLURGY DIVISION
INORGANIC MATERIALS DIVISION

DIRECTOR APPLIED PHYSICS LABORATORY
UNIVERSITY OF WASHINGTON
1013 NORTHEAST FORTIETH STREET
SEATTLE WA 98105

METALS AND CERAMICS
INFORMATION CENTER
BATTELLE-COLUMBUS DIVISION
505 KING AVENUE
COLUMBUS OH 43201

METALS AND CERAMICS DIVISION
OAK RIDGE NATIONAL LABORATORY
P O BOX X
OAK RIDGE TN 37830

LOS ALAMOS SCIENTIFIC LABORATORY
P O BOX 1663
LOS ALAMOS NM 87544

ATTENTION REPORT LIBRARIAN

ARGONNE NATIONAL LABORATORY
METALLURGY DIVISION
P O BOX 229
LEMONT IL 60439

DISTRIBUTION LIST (Cont.)

BROOKHAVEN NATIONAL LABORATORY
TECHNICAL INFORMATION DIVISION
UPTON LONG ISLAND
NY 11973

ATTENTION RESEARCH LIBRARY

OFFICE OF NAVAL RESEARCH
BRANCH OFFICE
1030 EAST GREEN STREET
PASADENA CA 91106

DR E M BREINAN
UNITED TECHNOLOGY CORPORATION
UNITED TECHNOLOGY RESEARCH
LABORATORIES
EAST HARTFORD CT 06108

PROFESSOR H D BRODY
UNIVERSITY OF PITTSBURGH
SCHOOL OF ENGINEERING
PITTSBURGH PA 14213

MR R MORANTE
GENERAL DYNAMICS
ELECTRIC BOAT DIVISION
EASTERN POINT ROAD
GROTON CT 06340

PROFESSOR THOMAS W EAGAR
MASSACHUSETTS INSTITUTE
OF TECHNOLOGY
DEPARTMENT OF MATERIALS
SCIENCE AND ENGINEERING
CAMBRIDGE MA 02139

PROFESSOR D G HOWDEN
THE OHIO STATE UNIVERSITY
DEPARTMENT OF WELDING
ENGINEERING
190 WEST 19TH AVENUE
COLUMBUS OH 43210

DR C S KORTOVICH
TRW INCORPORATED
23555 EUCLID AVENUE
CLEVELAND OH 44117

PROFESSOR K MASUBUCHI
MASSACHUSETTS INSTITUTE
OF TECHNOLOGY
DEPARTMENT OF OCEAN
ENGINEERING
CAMBRIDGE MA 02139

PROFESSOR J W MORRIS JR
UNIVERSITY OF CALIFORNIA
COLLEGE OF ENGINEERING
BERKELEY CA 94720

DR NEIL E PATON
ROCKWELL INTERNATIONAL
SCIENCE CENTER
1049 CAMINO DOS RIOS
P O BOX 1085
THOUSAND OAKS CA 91360

MR A POLLACK
NAVAL SHIPS RESEARCH AND
DEVELOPMENT CENTER
CODE 2821
ANNAPOLIS MD 21402

PROFESSOR W F SAVAGE
RENSELAER POLYTECHNIC INSTITUTE
SCHOOL OF ENGINEERING
TROY NY 02181

PROFESSOR O D SHERBY
STANFORD UNIVERSITY
MATERIALS SCIENCES DIVISION
STANFORD CA 94300

DR G ECER
WESTINGHOUSE ELECTRIC CORPORATION
RESEARCH AND DEVELOPMENT CENTER
PITTSBURGH PA 15235

DR C R WHITSETT
MCDONNELL DOUGLAS RESEARCH
MCDONNELL DOUGLAS CORPORATION
ST LOUIS MO 63166

DISTRIBUTION LIST (Cont.)

DR J C WILLIAMS
CARNEGIE MELLON UNIVERSITY
DEPARTMENT OF METALLURGY
AND MATERIALS SCIENCES
SCHENLEY PARK
PITTSBURGH PA 15213

MR I CAPLAN
DAVID W TAYLOR NAVAL SHIP
RESEARCH AND DEVELOPMENT
CENTER
CODE 2813
ANNAPOLIS MD 21402

DR G R LEVERANT
SOUTHWEST RESEARCH INSTITUTE
8500 CULEBRA ROAD
P O BOX 28510
SAN ANTONIO TX 78284

NAVAL ELECTRONICS LABORATORY
SAN DIEGO CA 92152

ATTENTION ELECTRON MATERIALS
SCIENCES DIVISION

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY	4
RESULTS AND DISCUSSION	8
Metallographic Studies of Weld Metals	9
Electron Microprobe Examination	9
Optical Metallographic Examination	9
Chemical Analysis of Weld Metal	18
Determination of Rare Earth Hydrogen Gettering Capability	18
Purpose of Button Melting Tests	21
Residual Gettering Ability of Weld Metals	22
AX-140 and L-140 Filler Wires	22
Rare-Earth Silicon and Rare-Earth Nickel Wires	29
Different Levels of Hydrogen Contamination	29
Rare-Earth Nickel Wire and Iron Powder	29
Effect of Premelting in Argon and Argon-2% O ₂	29
Protection From Deoxidation by Aluminum Addition	33
Rare Earth Additions in Submerged-Arc Welds	33
Experimental Procedure	34
Submerged-Arc Weld Test Results	35
CONCLUSIONS AND RECOMMENDATIONS	41
REFERENCES	45

ACKNOWLEDGEMENTS

The work performed under this contract was supported and monitored by the Office of Naval Research, Metallurgy Program directed by Dr. A. M. Diness. This support is appreciated together with that of Dr. Bruce A. MacDonald (ONR, Arlington) and Dr. George Sandoz (ONR, Chicago) both of whom provided a personal interest.

In addition, the assistance of Mr. A. Pollack, NSRDC, in providing HY-130 base plate and welding wire is greatly appreciated. The prompt delivery of special cored welding wires by Hobart Brothers Company aided greatly in the progress of the program.

HYDROGEN IN HY-130 WELD METAL

by

Michael D. Hayes and Daniel Hauser

INTRODUCTION

This program was established with the objectives of studying hydride forming materials and their gettering ability in a steel weldment system; investigating the effect of getter materials on gas metal-arc welding (GMAW) metal transfer and getter material transfer efficiency; and investigating the effect of getter elements on the mechanical properties of HY-130 welds made with hydrogen contamination.

Hydrogen can cause cracking in both the weld heat-affected zone and weld metal of high yield strength steels. In these steels, delayed cracking results from the presence of hydrogen in combination with a hard microstructure and tensile residual stresses. Exploratory and advanced development efforts, however, have not indicated a sensitivity to heat-affected-zone cracking in HY-130 steel. Hydrogen levels insufficient to cause cracking can decrease ductility and especially reduction of area in a tensile test.

The shielded metal-arc welding (SMAW) process requires stringent procedural controls to minimize the hydrogen-related strain effects. However, welding procedures have been developed that meet qualification and specification requirements for SMAW, gas metal-arc welding (GMAW), and gas tungsten-arc welding (GTAW) of HY-130 steel. Thermal requirements for production welds have been established, and there are indications that the use of a combination of 300 F preheat and postheat is effective in lowering the diffusible hydrogen content of weldments. In shielded metal-arc welds made at either 40 KJ/in or 30 KJ/in, energy input, less than 2.5 ppm of diffusible hydrogen was measured and no cracking was observed. In practice, however, it may be difficult to control the amount of moisture in SMAW electrode coatings and subsequently maintain the diffusible hydrogen content below 2.5 ppm. For

example, new coating formulations with extra low moisture content (the specification calls for 0.1 weight percent) are partially successful but problems of embrittlement of the coating (causing increased susceptibility to spalling), and the pickup of moisture from humid atmospheres present operational concerns. Although shielded metal-arc welds are most sensitive to embrittlement, gas metal-arc welds have also shown inconsistent ductility results on occasion. These occurrences have usually been related to "dirty" wire being used for welding.

Extensive precautions have been required for the control of hydrogen in both processes to obtain welds with adequate properties, and these precautions are not easily obtainable in a shipyard environment. It appears that this technology has been pushed to its limit and there is a need for a new approach.

The present program is directed at providing a new approach to the hydrogen embrittlement problem; that is, one in which the idea is to tolerate reasonable amounts of hydrogen contamination in the weld, but then to render the gas innocuous by chemically tying up the gas in the form of a hydride.

In order to appreciate how the hydrogen could be effectively "gettered" in the weldment, an understanding of the hydrogen absorption mechanism in weld pools is needed.

Hydrogen, which is present in most arc-welding systems, emanates from contamination - electrode coatings and hydrated oxides or oil contamination on the surface of the plate or filler wire. The gas is dissociated and ionized in high-temperature regions of the arc (30,000 K) and is transported to the molten surfaces of the pool and wire by high velocity plasma jets existing in the arc. At the relatively low temperature (3000 K) adjacent to the molten metal surfaces, the hydrogen reassociates to a large extent and is absorbed by the molten metal according to Sievert's law for the solution of molecular gases in metals. The amount absorbed is controlled by the partial pressure of molecular hydrogen at the liquid metal surface and the solubility of hydrogen in the liquid at the prevailing temperature. According to Howden and Milner,^{(1)*} the effective temperature of the liquid metal beneath the arc is about 2100 C so that the solubility of hydrogen in iron is estimated at 40 ml/100 gm. Due to the violent stirring action of the current passing through the weld pool, it is

* References are given at end of this report.

thought that the whole pool becomes saturated with gas corresponding to this high-temperature solubility. On solidification, little gas is expelled so that the high-temperature austenitic structure becomes supersaturated with hydrogen. Gas is then lost by solid state diffusion of hydrogen through the weld surface and to the heat-affected zone of the weld. This process continues until on cooling, the austenitic weld metal transforms to ferrite or martensite in the case of HY-130. Ferrite and martensite have much lower hydrogen solubilities than austenite and so the supersaturation or "internal solution pressure" is greatly increased. This supersaturation of hydrogen combined with high-strength structures and tensile shrinkage stresses in the weld produces cracking and embrittlement. If the hydrogen could be chemically combined in the form of a hydride, the high internal solution pressures of hydrogen would not exist and it is possible that the embrittlement or cracking would not occur. It is highly desirable, however, that the hydride be unstable at high temperatures so that escape of excess hydrogen can occur by diffusion as is normal. On the other hand, it is also desirable that the hydrides become stable prior to transformation of the austenite to martensite so that there is *no diffusible* hydrogen at this stage. Fortunately, this is the nature of most metallic hydrides.

The hydride stability of selected elements may be compared on a relative basis by the value of their dissociation pressure. These values are known for pure hydrides but may not be as reliable for solutions of these elements in steel, depending upon the effect of other elements in the steel on the activity of the hydrogen getter. If it is presupposed that the more effective getters would form stable hydrides at temperatures where the weld metal or steel is still in the austenitic form, during cooling or at least prior to full transformation, then the elements Ca, Ce, La, Pr, Sr, and Y appear best.

Compatibility of these elements with iron was reviewed and, based on limited data, their solubility is generally low in both austenitic and ferritic iron. At least one intermetallic compound exists in the Fe-Ce system. It is difficult to forecast how effective these elements will be from a metallurgical point of view since distribution of the getter may be important. For example, if the element were to be in solid solution, efficient gettering may be expected due to the close proximity of the element with the hydrogen in solution. On the

other hand, the mobility of hydrogen in high-temperature iron is so great that the element in segregated form may be just as effective.

Based on this information, it appears that misch metal is of most interest based on the fact that it contains large proportions of Ce, La, and other rare earth elements including Y and Pr. In addition, misch metal additions are made commercially to steel and, therefore, the technology is reasonably well established.

In one study,⁽²⁾ additions of lanthanum and cerium were made to a high-strength steel to getter hydrogen. Rare-earth content was varied from 0.03 to 0.17 weight percent. At high rare-earth concentrations (0.15 weight percent) hydrogen embrittlement resistance was improved in delayed failure tests. Mechanical properties were reported to be adequate with the exception that the Charpy impact toughness decreased. This was attributed to the formation of continuous rare-earth oxide inclusions at prior austenite grain boundaries.

SUMMARY

The first year's work⁽³⁾ concentrated on evaluating the gettering ability of misch metal which contained about 50 percent cerium, lanthanum and small quantities of other rare earths, and determining a practical method of adding the rare earths to the weld pool. By the end of the first year, welds had been made with rare-earth additions and arc-transfer characteristics had been studied.

It was shown that an addition of 0.2 weight percent misch metal could tie up the residual hydrogen typical of that remaining in a weld with 5 percent hydrogen contamination. Rare-earth hydrides were shown to be suitable, in terms of stability, for a welding system. Dissociation temperatures were about 760 C meaning that as a weld is made, the hydride is unstable on cooling from the solidification temperature to about 760 C. During this cooling period, hydrogen gas can diffuse freely in the solid state and escape through free surfaces to reduce the concentration of hydrogen in the weld. Below 760 C, however, the hydrogen will combine with the getter materials at a temperature higher than the M_s temperature of most hardenable steels. This

means that any hard microstructures formed by transformation will not be exposed to diffusible hydrogen, thereby precluding weld cracking and embrittlement.

Filler metals containing rare earths were produced by adding misch metal to a remelted ingot of HY-140 filler metal in a vacuum induction furnace. Transverse cracking problems developed during the rolling and drawing of the ingots into wire. Wires with diameters less than 3/8 inch (9.53 mm) could not be produced with rare earth contents above 0.045 weight percent. Metallographic studies of the cracking problem indicated the cause to be a low melting point eutectic structure formed by misch metal and iron. This segregated phase and the cracking were intergranular with initial internal cracks developing during hot working and propagating with subsequent cold rolling and drawing.

The effect of rare earth additions on arc characteristics was studied by high-speed photography of bead-on-plate welds. The films, at 1000 frames per second, did not indicate any deleterious effect of the rare-earth addition on arc characteristics. These studies emphasized the effect on drop transfer and did not address the equally important aspect of arc stability or arc wandering. Later observations of the arc have indicated arc instability when rare earths are added, and in particular "cathode attachment" to rare earths in the puddle.

The transfer efficiency of the rare-earth components in the wire is very important in that a compensation for losses in the arc, or in the weld pool, must be compensated by an addition to the wire. Investigation of the transfer efficiency of cerium in the GMAW system for shielding gases of both argon and argon/2 percent oxygen indicated that the recovery efficiency was between 10 to 20 percent for a bead-on-plate weld. Such a low transfer efficiency can create problems both in wire production and in the weldment. In order to obtain the required (for complete hydrogen gettering) levels of rare earths in the weld metal, 5 to 10 times that amount must be added to the wire. This could cause hot shortness problems in wire production. The rare earth "lost" in the transfer could end up as nonmetallic inclusions or intergranular phases detrimental to weldment properties and ineffective as hydrogen getters. The most obvious reason for a loss would be oxidation of the rare earth by the oxygen in the shielding gas or in the weld metal. This loss mechanism was substantiated by the presence of a black tenacious slag on the weld bead surface when argon/2 percent oxygen was used as the shielding gas. However, this slag was not chemically analyzed.

During the second year of the program,⁽⁴⁾ efforts were concentrated towards perfecting a method of producing electrode wires containing a pure misch metal core and utilizing a commercially fabricated experimental electrode wire having a rare earth silicide core.

The successful fabrication of misch metal-steel composite welding wire, produced by sealing of misch metal in the core of a drilled-out steel bar, was not realized because of cracks that developed in the wire during the rolling and drawing operations. These cracks appeared to initiate from fins formed and rolled into the surface during the rolling operation. The cracks thus formed resulted in wire with continuous longitudinal splits. A second contributing factor was the low temperature used in the heat-treat cycle; it was not high enough to remove prior cold work in the steel, thus making it more susceptible to crack propagation. Measures designed to overcome the difficulties encountered have been outlined but not pursued.

The specially made electrode wire having a rare-earth silicide core rather than misch metal was evaluated by cold-wire addition to welds being made with Airco AX-140 electrode wire. Several problems were encountered. Hydrogen gettering tests showed that silicon did not reduce the potency of the rare earths present. But, adding it resulted in a weld metal containing over 0.50 percent silicon. These welds showed significant reduction in notch toughness when compared to welds made without the additions. Therefore, work toward identifying additions that would not adversely influence mechanical properties was indicated. Both the silicon content of the wire and the method of addition seemed to be causes of these problems.

The third year's effort⁽⁵⁾ on this program was aimed at the development and evaluation of rare earth cored electrode wires that did not contain silicon. Also, a weld metal cracking test that could be used to economically evaluate the crack susceptibility of experimental weld metals was evaluated and found to be unsuitable for this program.

The rare-earth silicide in the cored wire was replaced by a rare-earth nickel powder alloy that was commercially available from NOVAMET of Waldwick, New Jersey. It is composed of 68 percent nickel, 32 percent rare-earth materials (approximately 50 weight percent cerium, 50 weight percent without lanthanum) and minor trace elements. The first cored wire produced

was designed to contain 10 percent rare earth metal-nickel powder and 10 percent iron powder, with the remaining wire weight made up by a low carbon sheath. It was determined that this first heat of wire had been baked in air at 600 F (315 C) to deactivate or remove lubricants during the manufacturing process. This oxidized the rare earths and rendered the wire ineffective as a hydrogen getterer.

The next lot of wire (No. FF8-115-3) was prepared without baking and the results of hydrogen gettering tests indicated that the contained powder was capable of tying up the diffusible hydrogen. The third lot of the rare earth-nickel cored wire (FF8-115-4) was fabricated with an iron powder addition using the same "no-bake" procedure and also proved capable of gettering hydrogen.

A brief study was made of the gapped-bead-on-plate cracking test to determine if it was feasible for this program. The results indicated that the test was not suitable for gas metal-arc welding as used in this program. The major reasons for this were the higher heat inputs used in this program, less massive heat sinks and a lower quantity of hydrogen than those used in the development of this test. Susceptibility to hydrogen cracking was also evaluated with spot fusion tests, restrained V-groove tests, and bead-on-plate tests. The restrained V-groove test was satisfactory to show transverse delayed cracks when hydrogen was present in the shielding gas. The bead-on-plate tests were very useful for illustrating the tendency to encounter hot cracking when the rare-earth content exceeded 0.10 percent using pure argon shielding gas.

The results of weld tests conducted to evaluate the transfer efficiency of the rare-earth nickel, and the residual rare earth present in welds that was available to getter hydrogen, indicated that the use of argon-2 percent oxygen shielding gas oxidized the rare earth addition. Welds made under pure argon contained residual rare earths and could still getter hydrogen. However, welds made with pure argon shielding gas exhibited hot cracking and a poor bead shape.

The effect of the rare earth nickel additions on mechanical properties was evaluated by preparing V-groove specimens for impact testing. The rare earths were added to the weld by cold feeding the cored wire into the leading edge of the weld pool. The impact strength of the rare-earth nickel-containing welds is lower at room temperature than that obtained with rare-

earth silicide additions. It became evident that the weld metal notch toughness is reduced when rare-earth elements are added to weld metal. The greater loss of toughness of the rare-earth nickel welds versus the rare-earth silicon welds was attributed to greater oxidation of the rare-earth nickel compounds and the resultant oxide inclusions. This was somewhat substantiated by spheroidal compounds present within the grains, and a loss of the ability to getter hydrogen.

The results of the third year's work indicated that in order to transfer enough rare earths to getter hydrogen, gas metal-arc welding must be carried out using a pure argon shield. Welding performance characteristics when using pure argon were poor with arc instability, excessive spatter, and irregular weld bead profiles. Further metallurgical investigation was also deemed necessary to discover why the rare-earth nickel welds had low impact strengths.

During the fourth year of the program, which is the subject of the rest of this report, the major effort has been aimed toward gaining an understanding of the effects that had been observed during the previous three years. This effort included metallographic and microprobe analyses of welds that had been produced, and a detailed hydrogen gettering analysis of various wires and weld metals. Several welding parameter variations were investigated in order to improve rare-earth transfer in the gas metal-arc process.

Finally, a successful method of utilizing the rare-earth wires was discovered in a series of submerged-arc weld tests. The use of a rare-earth nickel-cored wire as a second cold-wire addition proved capable of preventing hydrogen cracking when water-saturated flux was used. A weld made under identical conditions without the rare-earth addition exhibited classic delayed hydrogen cracking.

RESULTS AND DISCUSSION

In the following sections, the experimental procedures, results, and discussion of the fourth year's work are presented.

Metallographic Studies of Weld Metals

Electron Microprobe Examinations

The first investigation that was conducted was an electron microprobe study of one of the previous welds that had exhibited low mechanical properties, most notably lower impact strength than other welds made with identical conditions. The parameters and properties of these welds are shown in Table 1. Weld metal from Weldment V-9 was chosen for investigation. The fracture surfaces of Charpy specimens from the weldment were observed to contain a dark foreign material resembling an oxide. Therefore, a section of a broken Charpy specimen was prepared for microprobe investigation. The specimen was sectioned as shown in Figure 1 so that base metal, heat-affected zone (HAZ) and weld metal could all be examined. The purpose of the microprobe examination was to determine if any rare-earth materials transferred to the weld metal and what the material on the fracture surface was. The sample was mounted and then polished using a diamond powder to avoid injecting rare-earth materials with an alumina abrasive. Areas of major inclusions were first found with an optical microscope and noted for further study with the microprobe.

Microprobe examination did not reveal the presence of any rare-earth compounds in the weld metal. Most of the inclusions were silicates, calcium compounds, and small amounts of FeO and Al₂O₃. The areas near the fracture surface that were in the plane of focus of the probe contained a number of silicate inclusions, indicating that the material on the fracture surface was also a silicate material. No areas containing silicate inclusions were found in the base metal or HAZ. The source of the silicate inclusions was not determined.

Optical Metallographic Examinations

It is known that rare-earth compounds can affect the welding arc through a change in the ionization state of the plasma. Any resultant change in arc energy would be expected to be manifested in a change in weld metal nugget area (cross-sectional area of molten metal produced in one pass - including filler metal and remelted weld metal and base metal in multipass weldments), and weld metal -HAZ hardness.

TABLE 1. WELDING PARAMETERS AND IMPACT RESULTS OF FOUR V-GROOVE WELDS

Weld No.	Specimen Length, in. (mm)	Current, Amps	Voltage, V	Steel Wire Feed ipm (m/min)	Rare Earth Wire Feed, ipm (m/min)	Travel Speed ipm (m/min)	Calculated Rare Earth Additions, Percent	Actual Rare Earth Additions, Percent	Impact Strength (5)	
									CVN 30° F	ft/lbs 77° F
V-5	8(203)	348	23.0	(1) 178(4.52)	(3) 22(0.56)	14(0.36)	0.31	0.112	46	47
V-7	8(203)	356	22.5	(2) 178(4.52)	(3) 38(0.97)	11(0.28)	0.51	--	32	35
V-8	8(203)	357	23.8	(2) 184(4.67)	(4) 56(1.42)	12(0.30)	0.40	0.054	35	38
V-9	19(457)	356	23.7	(2) 180(4.57)	(4) 56(1.42)	12(0.30)	0.40	0.028	22	27

Note: Shielding gas - Argon + 2 percent O₂ at 40 cfh (1.13 m³/h) -- contact tube to work distance 0.5-inch (12.7 mm).

(1) AX-140 welding wire Airco; 0.0625-inch (1.59 mm) diameter.

(2) 140 S welding wire Linde; 0.0625-inch (1.59 mm) diameter.

(3) Rare earth containing wire Lot Number FF8-115-3.

(4) Rare earth containing wire Lot Number FF8-115-4.

(5) Spectrographic analysis of pad made under identical welding parameters.

Inclusions investigated by microprobe were in cross-hatched area.

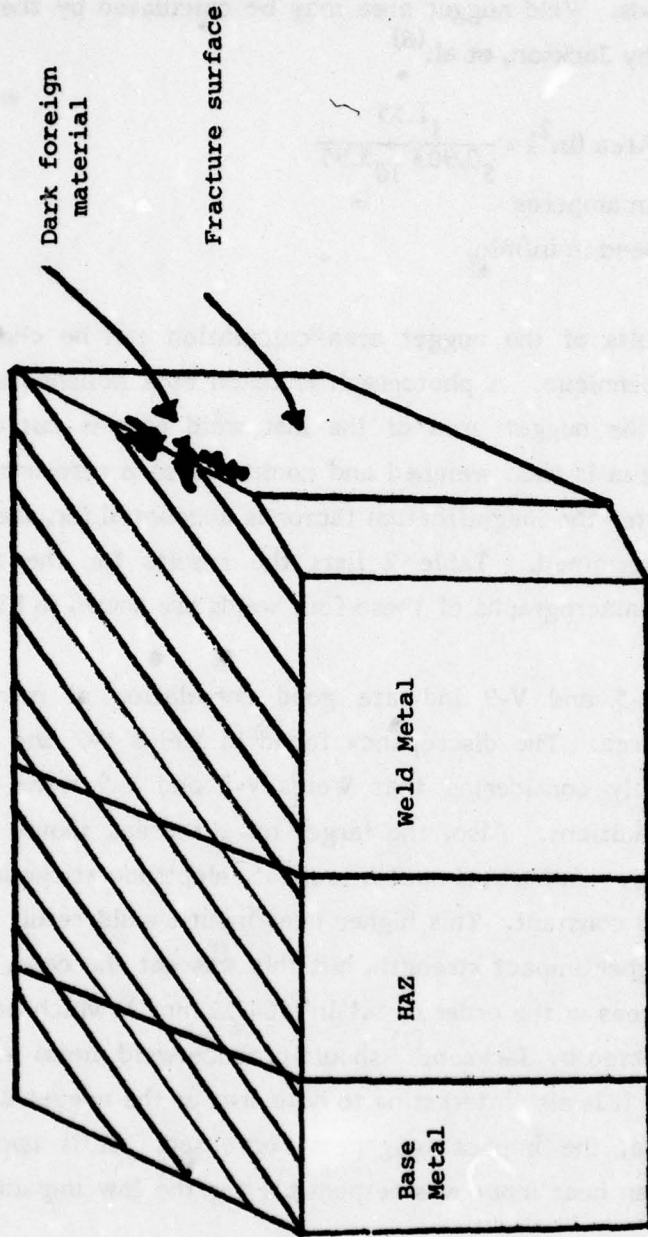


FIGURE 1. CROSS SECTION OF CHARPY SPECIMEN SHOWING AREA OF MICROPROBE EXAMINATION

These effects were determined analytically and then checked by experimental methods. Weld nugget area may be calculated by the empirical equation developed by Jackson, et al:⁽⁶⁾

$$\text{Nugget Area (in}^2\text{)} = \frac{I^{1.55}}{S^{0.903} 10^{3.95}}$$

where I = current in amperes

S = travel speed in in/min.

The results of the nugget area calculation can be checked by a photogravimetric technique. A photograph is taken of a polished and etched cross section and the nugget area of the last weld pass is cut out of the photograph. This area is then weighed and compared to a reference piece of the photograph. After the magnification factor is accounted for, the true weld nugget area is determined. Table 2 lists the results for the four welds investigated. Photomicrographs of these four welds are shown in Figures 2, 3, 4, and 5.

Welds V-5 and V-9 indicate good correlation of measured and calculated nugget area. The discrepancy found in Welds V-7 and V-8 is not understood, especially considering that Welds V-8 and V-9 were made with nearly identical conditions. Also, the larger nugget areas should indicate a higher heat input, provided travel speed, preheat, electrode stickout, and wire feed rates remained constant. This higher heat input should result in a lower cooling rate and higher impact strength, but this was not the case. All of the welds had nugget areas in the order of 0.1 in² (64.52 mm²), which according to empirical data reported by Jackson,⁽⁷⁾ should produce weld metal with acceptable yield strength. It is also interesting to note that as the nugget areas of the four welds increase, the impact toughness decreased. It is apparent that something other than heat input was responsible for the low impact toughness values.

Results of the nugget area analysis were further supported by a hardness survey of the four welds. Hardness readings, in the weld metal, in the area where the Charpy specimens were extracted, averaged HRC 37 over a range of HRC 35-39. The indentations were made 60 mils apart, across the entire weld (both X and Y directions). No abnormally hard regions were encountered on any of the four weld cross sections.

TABLE 2. NUGGET AREAS OF WELDS MADE WITH RARE EARTH ADDITIONS

Weld	Nugget Area Calc., mm ² (in ²)	Nugget Area Measured, mm ² (in ²)	Percent Deviation
V-5	59.1612(0.0917)	61.7418(0.0957)	4.18
V-7	74.8386(0.1160)	61.3547(0.0951)	18.02
V-8	70.3870(0.1091)	57.7418(0.0895)	17.96
V-9	70.3870(0.1091)	69.6128(0.1079)	1.10



1% Nital Etch

4X

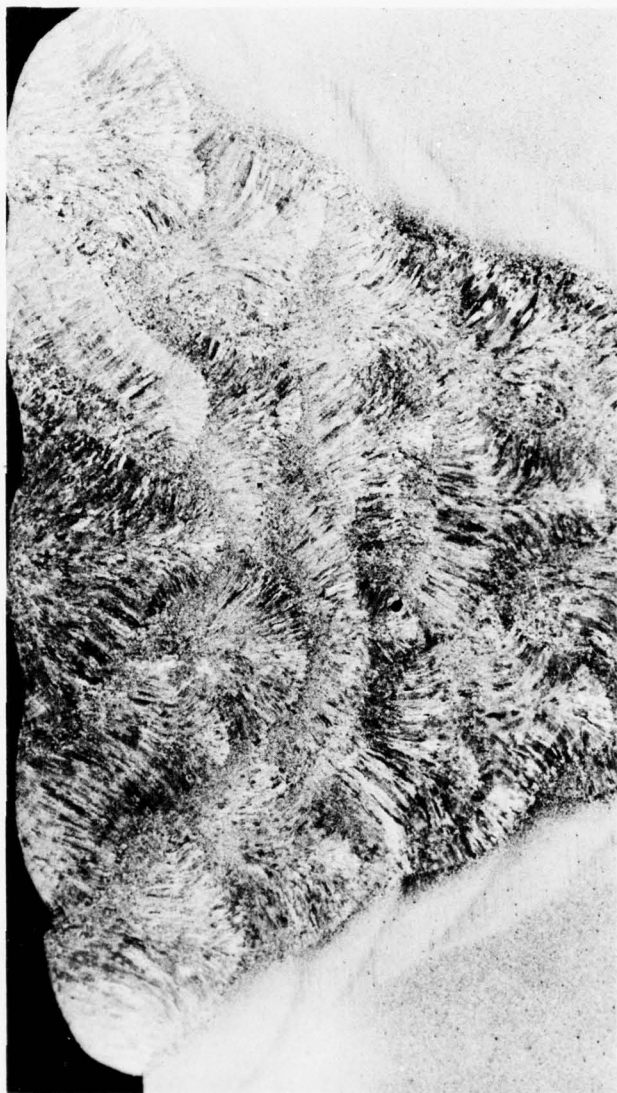
FIGURE 2. WELD V-5



4X

1% Nital Etch

FIGURE 3. WELD V-7



1% Nital Etch

4X

FIGURE 4. WELD V-8



4X

1% Nital Etch

FIGURE 5. WELD V-9

Chemical Analysis of Weld Metal

The largest difference in impact performance was between Welds V-5 and V-9. These welds were chosen for chemical analysis and sections from the welds were sent to a commercial testing laboratory. A chemical analysis was also made of the two filler wires used in these welds. The results of the analysis are shown in Table 3. The only significant difference in the weld metal chemistries was the higher aluminum content of V-5. It was suspected that Weld V-9 could contain too much nickel due to the rare-earth nickel filler wire addition. This was not indicated in the chemical analysis and, therefore, not deemed responsible for lower impact values. Also, the source of the excess silicon, detected in the microprobe investigation of V-9, was not established by chemical analysis.

Table 3 indicates one possible reason for the difference in impact strength and the silicate inclusions; the higher chromium in the AX-140 filler wire which was used for Weld V-5. This chromium could have tied up free oxides that were available to form silicates in V-9. It may have also prevented, or lessened, ferrous oxide formation on the filler wire, and thus reduced the free oxygen available in the weld pool.

Determination of Rare Earth Hydrogen Gettering Capability

Button-melting tests were conducted in order to determine the relative effectiveness of rare-earth silicide and rare-earth nickel compounds as hydrogen getterers. The apparatus and procedure for this test has been described in a previous report on this project.⁽³⁾ Basically, ten gram samples containing varied amounts of rare earths are melted with a gas tungsten arc (GTAW) under a shielding gas containing either 0.5 or 2.0 percent hydrogen. Prepurge, melting, and postpurge times are closely controlled. After the specimen has cooled below red heat, it is removed from the copper chill block and immediately water quenched and rinsed in alcohol. The specimen is then placed under an inverted funnel in a warm (150 F) glycerin bath. Hydrogen released from the specimen is collected in the closed neck of the funnel. The

TABLE 3. CHEMICAL ANALYSIS OF WELD METALS AND FILLER METALS

	Si	Mn	P	S	C	Ni	Cr	Mo	Cu	Al	V	Zr
Weld V-5	.26	1.38	.007	.010	.11	3.03	.64	.79	.05	.010	<.005	<.005
Weld V-9	.25	1.31	.005	.010	.10	3.10	.63	.78	.05	.005	<.005	<.005
Linde 140 S	.26	1.38	.010	.009	.11	2.32	.64	.78	.04	.0025	<.005	<.005
Airco AX-140	.35	1.74	.013	.010	.10	2.19	1.03	.60	.04	.001	<.005	<.005
HY-140 Base plate	.34	.84	.003	.007	.12	4.76	.49	.36	.06	.03	.08	.11

length of hydrogen gas column evolved may be optically measured. This measurement may then be converted into a volumetric measurement of evolved hydrogen. However, for relative comparisons the column length is sufficient.

Certain parameters in this hydrogen getting test require close observation in order to generate meaningful results. These are briefly discussed in the following paragraphs with mention of what errors could result from inaccurate methods.

The start, stop, and flow rate of the hydrogen-laden argon gas should be carefully controlled. In this work, the test was conducted in a closed chamber so the effect of cross-wind ventilation was absent. Also, the mix of the hydrogen and argon must be maintained. Commercial gases premixed in tanks were used in these tests. Following the supplier's recommended procedure, the tanks were slowly rolled on the floor for approximately 10 minutes prior to each set of tests.

It is important to choose an arc time that will melt all of the sample and yet not oversaturate the button with hydrogen. This time was determined to be 25 seconds for a ten-gram sample. The critical part of the test method became the technique for placing the specimens under the electrode, on top of the copper chill block, such that all of the sample melted after 25 seconds of arc time. Ten-gram samples of weld metal present no problem because they are small blocks that melt easily in a self-contained fashion. Most of the specimens, however, were prepared from filler wires, the 140-type wires, the rare-earth cored wires, and occasionally a third type of wire for other effects. These wires were usually cut into 1/2-inch (12.70 mm) long sections and then piled in a "firewood fashion" inside a 3/4-inch (19.05 mm) square "corral" fashioned from the high-strength filler wire. This corral was necessary to prevent the arc force from scattering the small wires. The weight of the corral was considered in the ten-gram sample because it was consumed in the melting.

The specimen transfer operation from the melting chamber to the glycerin must be accurately duplicated for comparable results. After the 65-second postpurge, during which the specimen cools below red heat on the copper chill block, the specimen must be quickly removed with a pair of laboratory forceps and quenched in cold water. The specimen is immediately removed from the water, rinsed in alcohol, quickly air dried, and then placed under an

inverted funnel in the glycerin. The entire time for these operations should be kept under 30 seconds.

The measurement of the hydrogen gas is made by visual comparison of the column length to a ruler graduated in millimeters. This is a relative measurement dependent upon the observer and the angle of observation (parallax). The observer should be constant and the angle of observation closely maintained to avoid large errors in measurement. In these tests each observer checked each result twice and then verified the results with an independent observer.

In order to determine the necessary length of time to leave the buttons under the funnel to trap all of the diffusible hydrogen, a series of tests were conducted. These tests used varied amounts of rare earths and two levels of hydrogen, 0.5 percent H₂ and 2.0 percent H₂. Hydrogen evolution was checked each 8 hours for 64 hours and increases were noted. No measurable change was detected in any of the samples after 24 hours. A closer check revealed that nearly all of the hydrogen evolved during the first 4 hours of the test, but the 24-hour mark was chosen for consistency and experimental convenience.

Purpose of Button Melting Tests

Button-melt hydrogen-gettering tests were conducted to provide answers to questions that had arisen during previous work and to investigate the cause of poor transfer of the rare-earth silicon and rare-earth nickel compounds to the weld metals. Specific tests were conducted to determine the following:

- o The ability of weld metals produced with the R.E.-Si and R.E.-Ni compounds to getter hydrogen after a prolonged period of time
- o The effect of using either the Airco filler wire (AX-140) or Linde filler wire (140S) in conjunction with either the R.E.-Si or R.E.-Ni cored wires
- o The relative ability of the R.E.-Si cored wire and the R.E.-Ni cored wires to getter hydrogen

- o The effect of two different levels of hydrogen concentration of the argon shielding gas
- o The gettering ability of the R.E.-Ni filler wire with and without iron powder added to the core
- o The effect of premelting the samples under an argon or argon-O₂ shielding gas before melting under the hydrogen laden gas
- o The possibility of protecting the rare earth from oxidation by adding aluminum to the premelt.

In tests during previous years, the weight of the sample button was not maintained constant. It was felt that this difference could cause a surface effect resulting in changes in the hydrogen absorption and release. In all the following tests, the button weight was maintained constant at 10 grams.

Data from these tests are presented in Tables 4 and 5. The specimens in Table 4 were only melted once, with the exception of the weld-metal samples, while Table 5 lists data from the dual-melt studies.

Residual Gettering Ability of Weld Metals

The results of Specimens 1-14 in Table 4 do not indicate that any of the weld metals, after remelting buttons in hydrogen-containing shielding gas, retained a residual gettering ability. Neither the level or type of rare earth seemed to have an effect. However, further tests described below indicate that the level of rare earths found in these weld metals was far below that necessary to getter hydrogen.

AX-140 and L-140 Filler Wires

Minor variations in results can be seen in Table 4, however, no major differences are observable between AX-140 and L140S filler wires. These results are plotted in Figures 6 and 7.

TABLE 4. RESULTS OF BUTTON-MELT HYDROGEN GETTERING TESTS

Comparison of: AX140 and L140 wire
 Rare earth silicon and rare earth nickel cored wires
 R.E.-Ni (FF8-115-3) without iron powder and R.E.-Ni (FF8-115-4) with iron powder
 0.5 and 2.0 percent hydrogen addition.

Specimen No.	Sample Material		Rare Earth, Percent	Percent H ₂ in Argon	Length of H ₂ Gas Column Evolved, (mm)	H ₂ Evolved Per Unit Weight, ml/g
	Total of 10 Gram Wt.	Sample Origin				
1	AX-140, R.E.-Si (392-6B)*	Weld 5-1	0.05	2.0	10	0.014
2	AX-140	Weld 6-1	0.00	2.0	14	0.020
3	AX-140, R.E.-Si (392-6B)	Weld 7-1	0.05	2.0	18	0.025
4	L 140 S, R.E.-Ni (FF8-115-3)	Weld V-5	0.112	2.0	10	0.014
5	L 140 S, R.E.-Ni (FF8-115-3)	Weld V-7	0.081	2.0	14	0.020
6	L 140 S, R.E.-Ni (FF8-115-4)	Weld V-8	0.054	2.0	13	0.018
7	L 140 S, R.E.-Ni (FF8-115-4)	Weld V-9	0.028	2.0	16	0.022
8	AX-140, R.E.-Si (392-6B)	Weld 5-1	0.05	0.5	6	0.008
9	AX-140	Weld 6-1	0.00	0.5	6	0.008
10	AX-140, R.E.-Si (392-6B)	Weld 7-1	0.05	0.5	5	0.007
11	L-140 S, R.E.-Ni (FF8-115-3)	Weld V-5	0.112	0.5	10	0.014
12	L-140 S, R.E.-Ni (FF8-115-3)	Weld V-7	0.081	0.5	8	0.011
13	L-140 S, R.E.-Ni (FF8-115-4)	Weld V-8	0.054	0.5	6	0.008
14	L-140 S, R.E.-Ni (FF8-115-4)	Weld V-9	0.028	0.5	6	0.008
15	AX-140, R.E.-Si (392-6B)	Filler wires	0.10	2.0	16	0.022
16	AX-140, R.E.-Si (392-6B)	Filler wires	0.20	2.0	14	0.020
17	AX-140, R.E.-Si (392-6B)	Filler wires	0.40	2.0	16	0.022
18	AX-140, R.E.-Si (392-6B)	Filler wires	0.80	2.0	0	0
19	AX-140	Filler wires	0.00	2.0	13	0.018
20	AX-140, R.E.-Si (392-6B)	Filler wires	0.40	2.0	14	0.020
21	AX-140, R.E.-Si (392-6B)	Filler wires	0.60	2.0	5	0.007

TABLE 4. (Continued)

Specimen No.	Sample Material		Sample Origin	Rare Earth, Percent	Percent H ₂ in Argon	Length of H ₂ Gas Column Evolved, (mm)	H ₂ Evolved Per Unit Weight, ml/g
	Total of 10 Gram Wt.	Sample					
22	AX-140	--	Filler wires	0	0.5	3	0.004
23	AX-140, R.E.-S1 (392-6B)		Filler wires	0.10	0.5	3	0.004
24	AX-140, R.E.-S1 (392-6B)		Filler wires	0.20	0.5	5	0.007
25	AX-140, R.E.-S1 (392-6B)		Filler wires	0.40	0.5	3	0.004
26	AX-140, R.E.-S1 (392-6B)		Filler wires	0.80	0.5	0	0
27	AX-140	--	Filler wires	0	0.5	3	0.004
28	AX-140, R.E.-S1 (392-6B)		Filler wires	0.40	0.5	5	0.007
29	AX-140, R.E.-S1 (392-6B)		Filler wires	0.60	0.5	0	0
30	L-140 S	--	Filler wires	0.00	0.5	6	0.008
31	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.10	0.5	5	0.007
32	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.20	0.5	5	0.007
33	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.40	0.5	3	0.004
34	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.60	0.5	1	0.001
35	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.80	0.5	1	0.001
36	L-140 S	--	Filler wires	0	2.0	13	0.018
37	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.10	2.0	11	0.015
38	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.20	2.0	10	0.014
39	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.40	2.0	11	0.015
40	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.60	2.0	3	0.004
41	L-140 S, R.E.-S1 (392-6B)		Filler wires	0.80	2.0	0	0
42	L-140 S	--	Filler wires	0	0.5	3	0.004
43	L-140 S, R.E.-N1 (FF8-115-3)		Filler wires	0.10	0.5	4	0.006
44	L-140 S, R.E.-N1 (FF8-115-3)		Filler wires	0.20	0.5	0	0
45	L-140 S, R.E.-N1 (FF8-115-3)		Filler wires	0.40	0.5	0	0
46	L-140 S, R.E.-N1 (FF8-115-3)		Filler wires	0.60	0.5	0	0
47	L-140 S, R.E.-N1 (FF8-115-3)		Filler wires	0.80	0.5	0	0

TABLE 4. (Continued)

Specimen No.	Sample Material		Sample Origin	Rare Earth, Percent	Percent H ₂ in Argon	Length of H ₂ Gas Column Evolved (mm)	H ₂ Evolved Per Unit Weight ml/g
	Total of 10 Gram Wt.						
48	L 140 S, --		Filler wires	0	2.0	11	0.015
49	L 140 S, R.E.-Ni (FF8-115-3)		Filler wires	0.10	2.0	13	0.018
50	L 140 S, R.E.-Ni (FF8-115-3)		Filler wires	0.20	2.0	3	0.004
51	L 140 S, R.E.-Ni (FF8-115-3)		Filler wires	0.40	2.0	0	0
52	L 140 S, R.E.-Ni (FF8-115-3)		Filler wires	0.60	2.0	0	0
53	L 140 S, R.E.-Ni (FF8-115-3)		Filler wires	0.80	2.0	0	0
54	AX-140, --		Filler wires	0	0.5	3	0.004
55	AX-140, R.E.-Ni (FF8-115-3)		Filler wires	0.10	0.5	5	0.007
56	AX-140, R.E.-Ni (FF8-115-3)		Filler wires	0.20	0.5	0	0.007
57	AX-140, R.E.-Ni (FF8-115-3)		Filler wires	0.40	0.5	0	0
58	AX-140, R.E.-Ni (FF8-115-3)		Filler wires	0.60	0.5	0	0
59	AX-140, R.E.-Ni (FF8-115-3)		Filler wires	0.80	0.5	0	0
60	AX-140, --		Filler wires	0	2.0	13	0.018
61	AX-140, R.E.-Ni (FF8-115-4)		Filler wires	0.10	2.0	17	0.024
62	AX-140, R.E.-Ni (FF8-115-4)		Filler wires	0.20	2.0	8	0.11
63	AX-140, R.E.-Ni (FF8-115-4)		Filler wires	0.40	2.0	0	0
64	AX-140, R.E.-Ni (FF8-115-4)		Filler wires	0.60	2.0	0	0
65	AX-140, R.E.-Ni (FF8-115-4)		Filler wires	0.80	2.0	0	0
66	L-140 --		Filler wires	0	0.5	4	0.006
67	L-140 R.E.-Ni (FF8-115-4)		Filler wires	0.10	0.5	4	0.006
68	L-140 R.E.-Ni (FF8-115-4)		Filler wires	0.20	0.5	2	0.003
69	L-140 R.E.-Ni (FF8-115-4)		Filler wires	0.40	0.5	0	0
70	L-140 R.E.-Ni (FF8-115-4)		Filler wires	0.60	0.5	0	0
71	L-140 R.E.-Ni (FF8-115-4)		Filler wires	0.80	0.5	0	0
72	L-140 --		Filler wires	0	2.0	10	0.014

TABLE 4. (Continued)

Specimen No.	Sample Material		Sample Origin	Rare Earth, Percent	Percent H ₂ in Argon	Length of H ₂ Gas Column Evolved (mm)	H ₂ Evolved Per Unit Weight ml/g
	Total of 10 Gram Wt.						
73	L-140 R.E.-N1 (FF8-115-4)		Filler wires	0.10	2.0	11	0.015
74	L-140 R.E.-N1 (FF8-115-4)		Filler wires	0.20	2.0	11	0.015
75	L-140 R.E.-N1 (FF8-115-4)		Filler wires	0.40	2.0	0	0
76	L-140 R.E.-N1 (FF8-115-4)		Filler wires	0.60	2.0	0	0
77	L-140 R.E.-N1 (FF8-115-4)		Filler wires	0.80	2.0	0	0

* Numbers in parenthesis indicate identification number of the rare earth-silicon and rare earth-nickel cored wires.

TABLE 5. HYDROGEN GETTERING TESTS WITH BUTTONS PREMELTED UNDER ARGON - 2% OXYGEN

Specimen No.	Specimen Origin 10 Grams Total Wt.	Material		1st Melt Gas	2nd Melt % H ₂	Rare Earth %	Length of Gas Column (mm)	H ₂ Evolved ml/g	
		Re. Desig	Matl. Form						
78	L-140 S	R.E.-Ni	FF8-115-3	Filler Wires	AR-202	0.5	0.4	11	0.015
79	L-140 S	R.E.-Ni	FF8-115-3	Filler wires	AR-202	0.5	0.4	3	0.004
80	L-140 S	R.E.-Si	392-6B	Filler wire	AR-202	0.5	0.8	4	0.006
81	L-140 S	R.E.-Si	392-6B	Filler wire	AR-202	0.5	0.8	4	0.006
82	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	AR-202	0.5	0.4	5	0.007
83	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	AR-202	0.5	0.4	4	0.006
84*	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	AR-202	0.5	0.4	4	0.006
85	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	AR-202	2.0	0.4	11	0.015
86	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	AR-202	2.0	0.4	14	0.020
87	L-140 S	R.E.-Si	392-6B	Filler wire	AR-202	2.0	0.8	14	0.020
88	L-140 S	R.E.-Si	392-6B	Filler wire	AR-202	2.0	0.8	11	0.015
89	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	Argon	2.0	0.4	10	0.014
90	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	Argon	2.0	0.4	10	0.014
91	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	Argon	0.5	0.4	2	0.003
92	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	Argon	0.5	0.4	3	0.004
93	L-140 S	R.E.-Si	392-6B	Filler wire	AR-202	2.0	0.8	11	0.015
94*	L-140 S	R.E.-Si	392-6B	Filler wire	AR-202	2.0	0.8	11	0.015
95*	L-140 S	R.E.-Ni	FF8-115-3	Filler wire	AR-202	2.0	0.4	21	0.029
Wt. % Al									
96	L-140 S	Aluminum	0	Filler wire	None	0.5	0.0	3	0.004
97	L-140 S	Aluminum	0	Filler wire	None	0.5	0.0	10	0.014
98	L-140 S	Aluminum	.01	Filler wire	None	0.5	0.0	5	0.007
99	L-140 S	Aluminum	.02	Filler wire	None	0.5	0.0	3	0.004
100	L-140 S	Aluminum	.20	Filler wire	None	0.5	0.0	3	0.004
101	L-140 S	Aluminum	.50	Filler wire	None	0.5	0.0	3	0.004
102	L-140 S	Aluminum	0	Filler wire	AR-202	0.5	0.0	6	0.008
103	L-140 S	Aluminum	0	Filler wire	AR-202	0.5	0.0	6	0.008
104	L-140 S	Aluminum	.01	Filler wire	AR-202	0.5	0.0	8	0.011
105	L-140 S	Aluminum	.02	Filler wire	AR-202	0.5	0.0	6	0.008
106	L-140 S	Aluminum	.20	Filler wire	AR-202	0.5	0.0	10	0.014
107	L-140 S	Aluminum	.50	Filler wire	AR-202	0.5	0.0	8	0.011

* 0.145 Grams of aluminum filler metal added to button during 1st melt to protect rare earth from oxidation.

Tests 96-107 conducted without rare earth addition to determine effect of Al on hydrogen absorption.

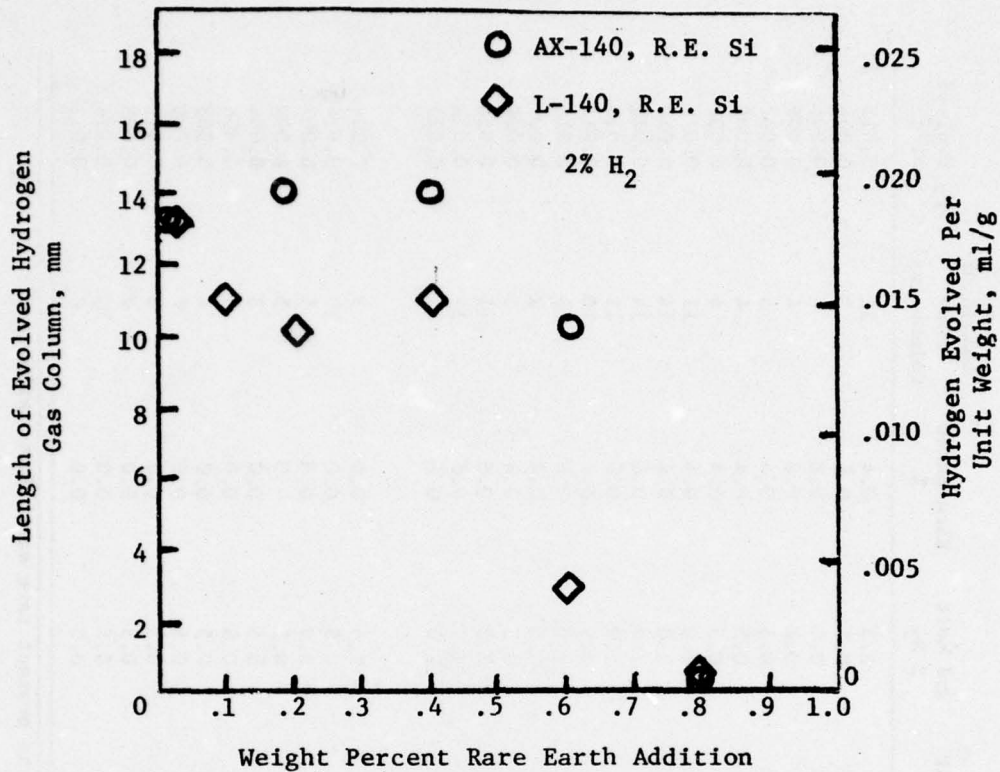


FIGURE 6. HIGH STRENGTH FILLER WIRE EFFECT ON H_2 GETTERING IN 2% H_2

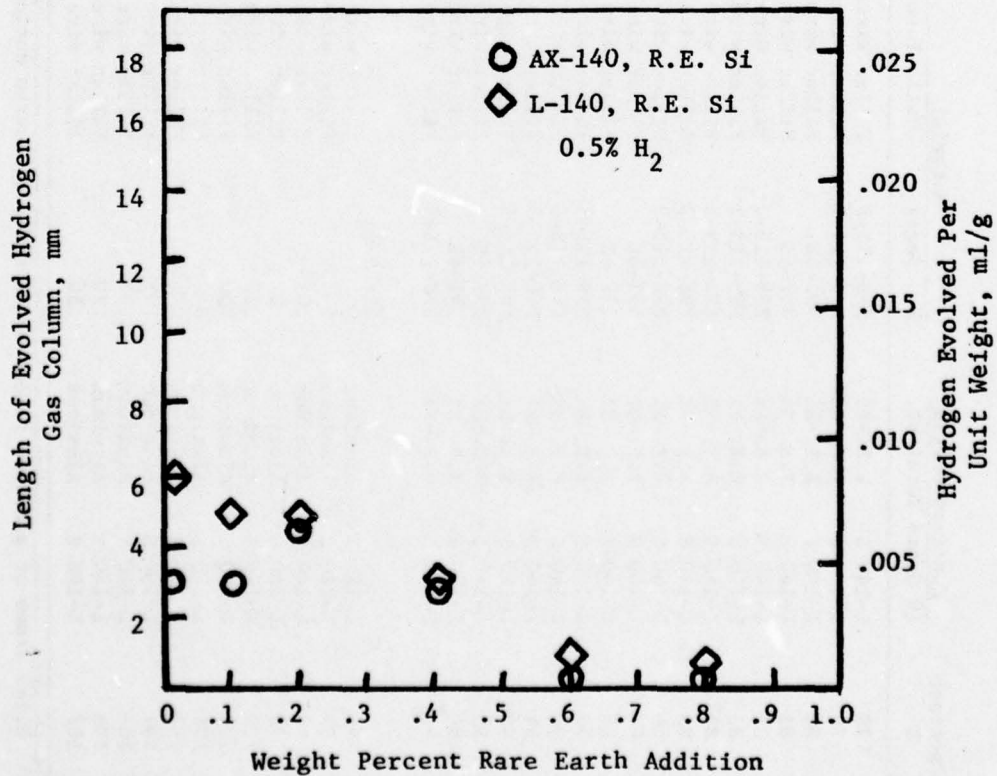


FIGURE 7. HIGH STRENGTH FILLER WIRE EFFECT ON H_2 GETTERING IN 0.5% H_2

Rare-Earth Silicon and Rare-Earth Nickel Wires

The rare-earth nickel-cored wires showed a superior gettering capability as compared to the rare-earth silicon wire. In the argon-2 percent hydrogen atmosphere, only 50 percent as much rare-earth nickel as rare-earth silicon was necessary to completely getter the melt. Figures 8, 9, 10, and 11 illustrate the capabilities of the different cored wires.

Different Levels of Hydrogen Concentration

Every one of the different rare-earth wire - filler wire combinations was tried at two levels of hydrogen addition, 0.5 percent and 2.0 percent. The variation in diffusible hydrogen released by the buttons corresponded quite well with the amount of hydrogen added. The 2.0 percent hydrogen level did not appear to oversaturate the button melt since all the hydrogen could be gettered in nearly every series of tests.

Rare-Earth Nickel Wire and Iron Powder

The rare-earth nickel wire without iron powder in the core (FF8-115-3) had a slightly better gettering ability than the wire with an iron powder addition (FF8-115-4). This difference was noticeable at the 0.20 percent rare-earth addition level in the 0.5 percent and 2.0 percent hydrogen addition. A comparison of these wires is plotted in Figures 12 and 13.

Effect of Premelting in Argon and Argon-2% O₂

These tests were conducted by premelting filler wires under argon and argon-0₂ before melting the resultant button under argon-H₂. The results of the button premelt tests are shown in Table 5. These results demonstrated the inability of the weld metals to getter hydrogen when remelted. There is some variation in the data, but the general trend indicates no residual gettering ability after premelting under argon or argon-2% O₂. This result for pure argon gas shielding was surprising in that the loss of rare earth in previous remelts of weld metals had been attributed to oxidation by oxygen in the shielding gas.

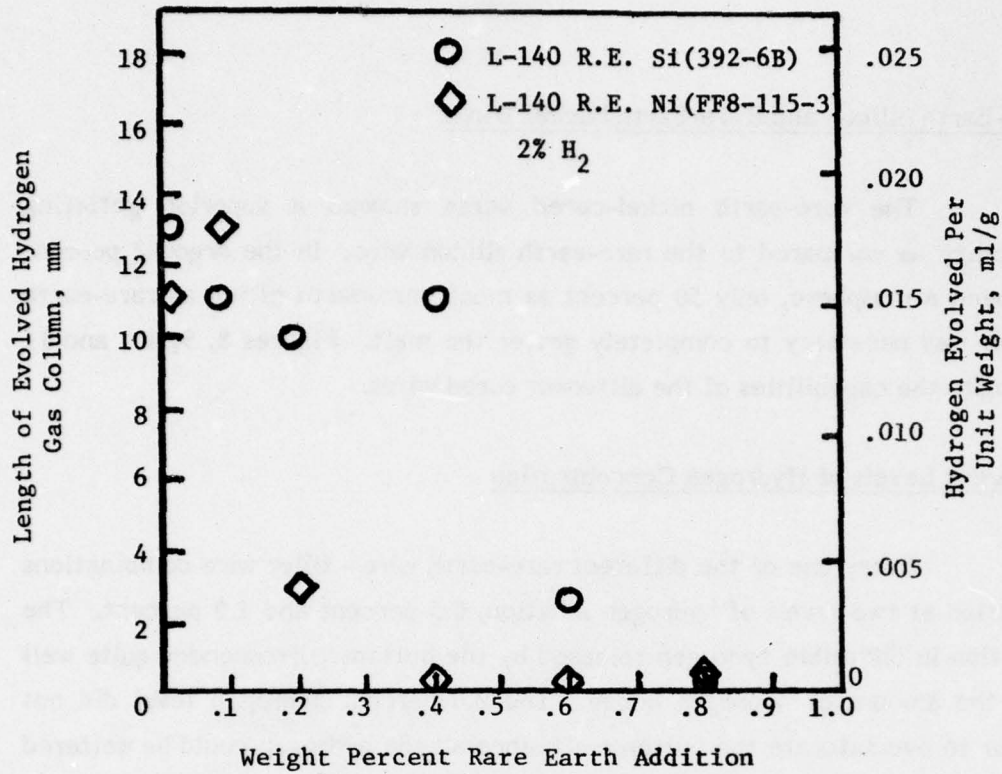


FIGURE 8. GETTER STRENGTH OF R.E. Ni, R.E. Si WIRES IN 2% H₂ WITH L-140 WIRE

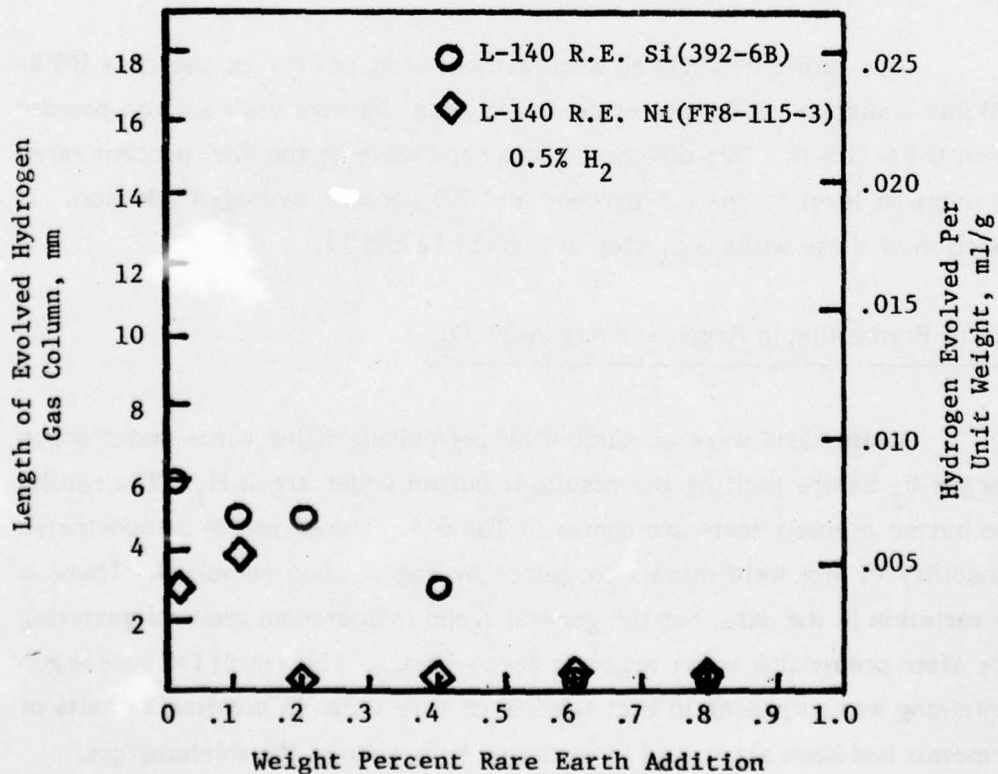


FIGURE 9. GETTER STRENGTH OF R.E. Ni, R.E. Si WIRES IN 0.5% H₂ WITH L-140 WIRE

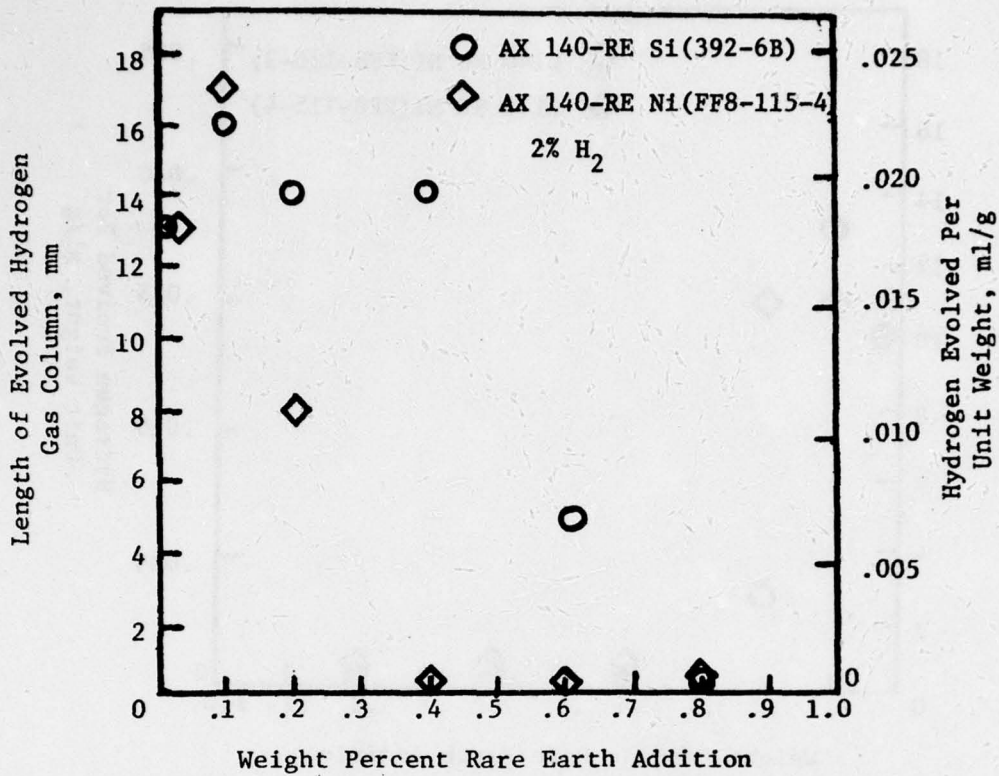


FIGURE 10. GETTER STRENGTH OF R.E. Ni, R.E. Si WIRES IN 2% H₂ WITH AX-140 WIRE

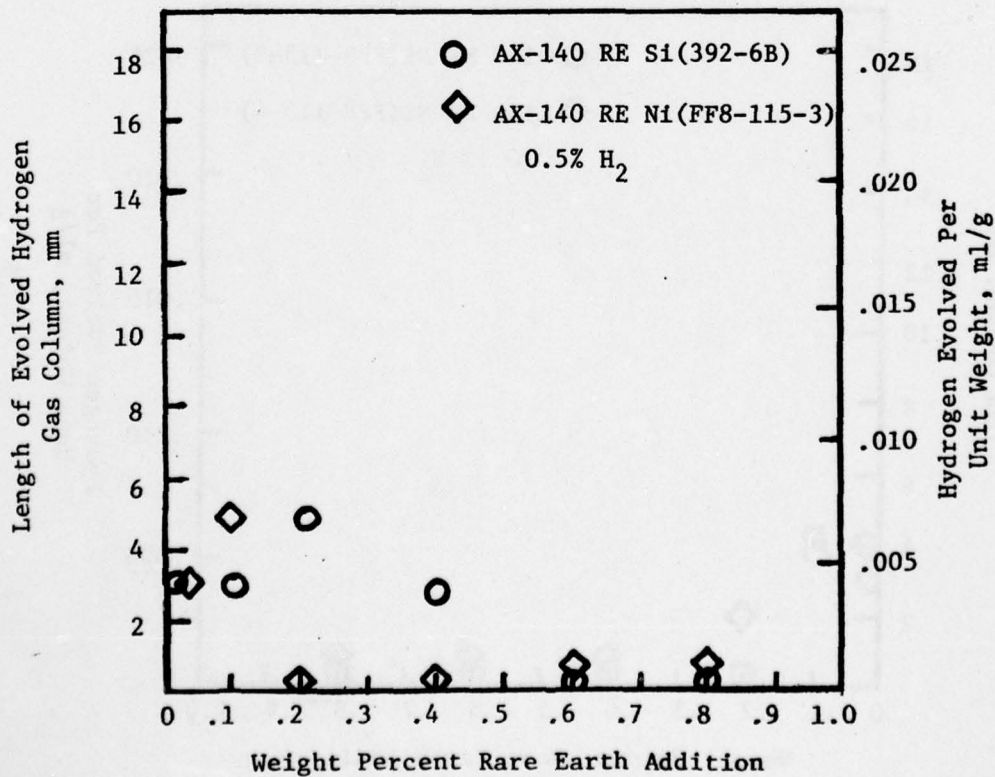


FIGURE 11. GETTER STRENGTH OF R.E. Ni, R.E. Si WIRES IN 0.5% H₂ WITH AX-140 WIRE

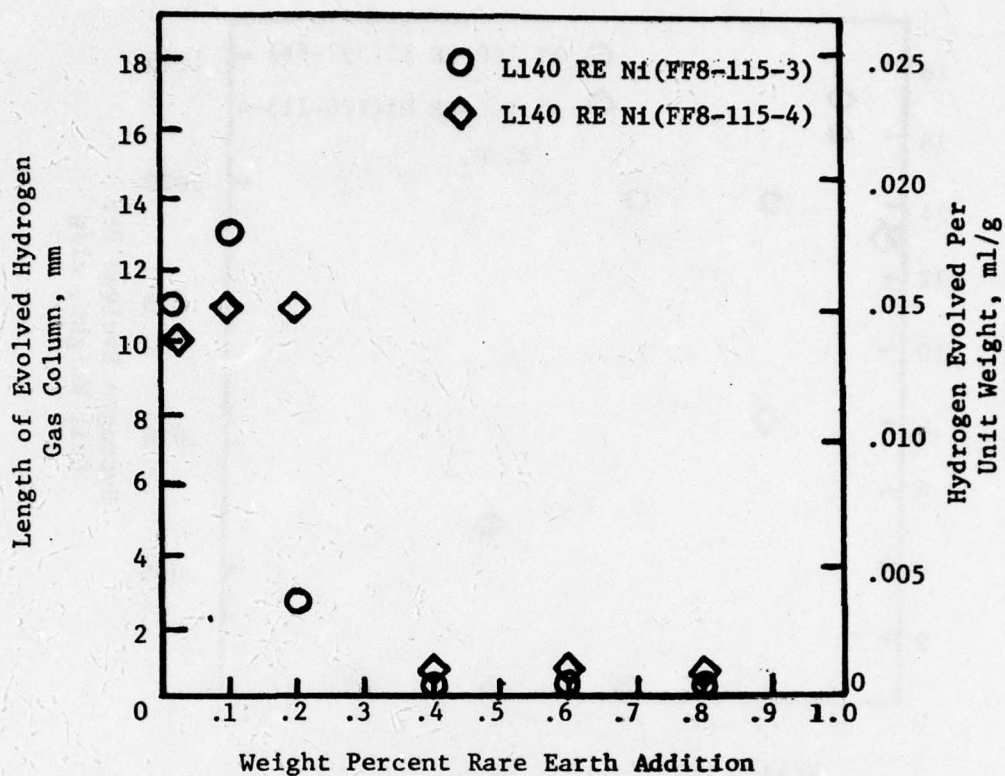


FIGURE 12. GETTERING STRENGTH OF R.E. WIRE WITH Fe POWDER (FF8-115-4), AND WITHOUT Fe POWDER (FF8-115-3), IN 2% H₂

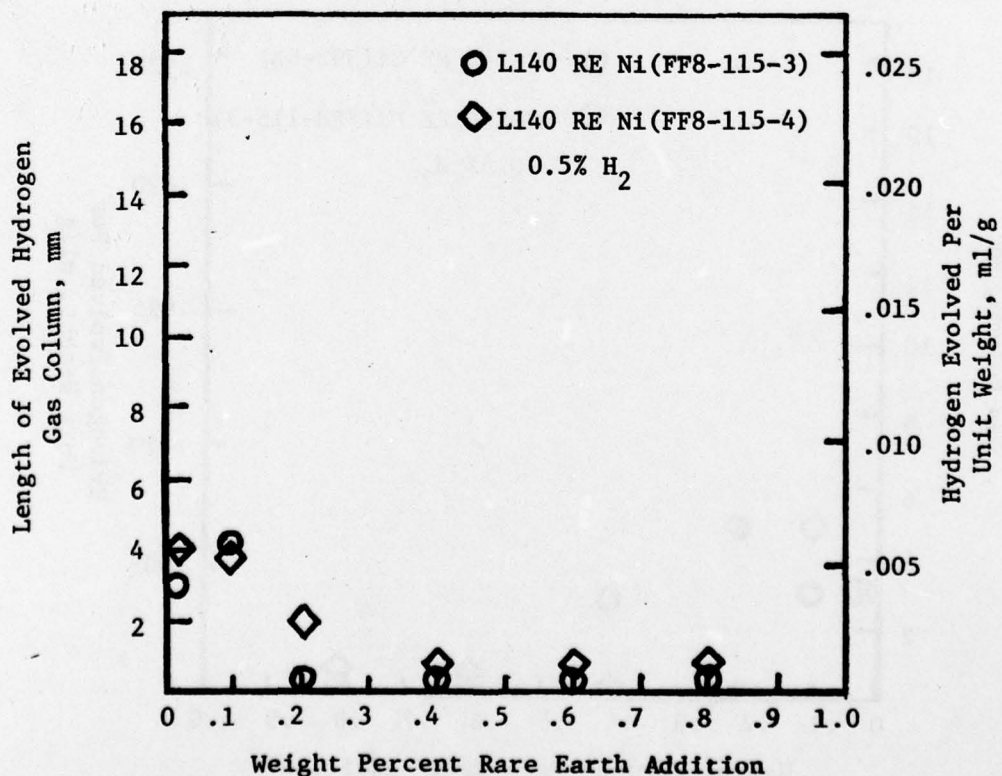


FIGURE 13. GETTERING STRENGTH OF R.E. WIRE WITH Fe POWDER (FF8-115-4) AND WITHOUT Fe POWDER (FF8-115-3) IN 0.5% H₂

Protection From Deoxidation by Aluminum Addition

Specimen Nos. 84 and 95 in Table 5 represent attempts to protect the rare earth from oxidation by adding aluminum for preferential oxidation. The results did not indicate any improvement in gettering ability. In fact, the level of hydrogen released by Specimen No. 95 was such a drastic increase that Tests 96-107 were conducted with aluminum only. The results of these tests showed no evidence of aluminum increasing or decreasing hydrogen pickup and release.

Clearly, the data from Tests 1 through 107 show considerable scatter. This is undoubtedly due to human inconsistency in the experimental procedure, since it can be seen that the scatter lies within each test set of six specimens. There is reasonably good correlation among duplicate sets of six specimens that were tested at different points in time. However, the trends are clear. In this respect, the button melting test provides a valuable approach to understanding hydrogen gettering.

Rare Earth Additions in Submerged-Arc Welds

The major problem that has appeared with the rare earths is finding a method for adding them to the weld pool. When rare earths were added to the pool in gas metal-arc welding with argon shielding the arc became unstable and poor welds resulted. Argon-oxygen shielding solved the arc instability problem, but all of the rare earths were oxidized and rendered ineffective as hydrogen getters.

The submerged-arc welding process (SAW) offers the advantage of a "protected arc", i.e., the arc is submerged beneath a layer of molten flux and shielding gas is not used. It was postulated that a rare-earth cored wire could be added to the submerged-arc weld pool without being oxidized. The optimum point of addition was theorized as just behind the advancing arc at the midpoint of the weld pool. This was believed to be necessary in order to prevent the rare-earth wire from melting before entering the pool and being absorbed by the slag. This concept was evaluated as described below.

Experimental Procedure

The experimental system consisted of a constant potential power supply, a side beam and carriage, and two wire feed systems. The lead wire (L140) was operated DCEP (reverse polarity). The rare-earth nickel cored wire (FF8-115-4) was operated as a cold-wire addition fed into the pool at a 30-degree angle from the vertical. The position of both filler wires was accurately established prior to making a flux cover.

The weight percent rare-earth addition was established by making trial welds and measuring the L140 wire-feed rate at the desired operating parameters. A rare-earth wire feed speed was then calculated to provide a percentage of the total filler wire addition. A 100-percent recovery of the rare earth in the weld metal was assumed for experimental purposes. The welding parameters were chosen based on past experimental submerged-arc welding of HY-130. Heat input was maintained at 45 KJ per linear inch and weld nugget area was maintained at 0.10 square inch.

Two conditions were varied in the experiment, the amount of rare earth added and the level of hydrogen present in the weld area. As previously mentioned the rare-earth addition was varied by changing wire-feed speed. The hydrogen content of the weld area was varied by changing the moisture level of the flux. The starting point was with a commercial fused flux that had been baked at 750 F for one hour. The first weld (V-10) was made with this flux and a large rare-earth addition (1.00 weight percent). The purpose of this test was to observe the effect of rare earths on the submerged arc. The next weld (V-11) was made with a rare-earth addition of 0.5 percent and a moisture laden flux. The flux was prepared by placing it in a humidity chamber at 100 F and 100 percent humidity for one hour. The third test (Weld V-12) was made with a 0.5 percent rare-earth addition, but the moisture level was increased by leaving the flux in the humidity chamber at 100 percent humidity and 100 F for 24 hours. In the fourth test (Weld V-13), the moisture level of V-12 was duplicated but no rare-earth addition was made.

These tests were designed to approximate actual working environment conditions in which a submerged-arc flux could be exposed to humid conditions for some length of time. Even though it was not possible to

determine the exact amount of diffusible hydrogen generated by this method, past experience has indicated that wet fluxes can lead to hydrogen cracking. Table 6 lists the parameters used on these four tests.

Submerged-Arc Weld Test Results

The first test, Weld V-10, indicated that rare-earth materials could be added to the submerged-arc weld pool without adversely affecting the arc, and resulting weldment appearance. Arc voltage and current, as measured by strip chart recorders, remained stable. The weld bead surface was smooth and free of undercut and spatter.

When moisture was added to the flux on Weld V-11, the bead surface became pock marked due to the large amount of steam generated. However, no delayed hydrogen cracking was observed in dye-penetrant examinations. Increased pock marking was observed on Weld V-12 at the higher moisture level but, again, no delayed cracking was found.

The high moisture content in the flux of Weld V-12 indicated that the rare-earth addition had gettered the hydrogen generated in the wet flux. Weld V-13 was produced without rare earths in order to verify this hypothesis. Pock marking was severe and similar to V-12. No delayed cracking was immediately indicated by dye-penetrant inspection.

It is known that hydrogen-induced cracking can occur long after the weld has cooled. Therefore, each of the plates was checked by dye penetrant weekly for six weeks. During this period of time, no cracks were found. After six weeks, all of the plates were radiographically inspected and transverse cracking was found in Weld V-13, the weld made with wet flux and no rare-earth addition. Positive prints of the radiographs from Welds V-10, V-11, V-12, and V-13 are shown in Figures 14, 15, 16, and 17, respectively. Porosity is apparent in all of the radiographs, but in 10, 11, and 12 it is small and dispersed in contrast to the large gas pores of Weld V-13. These welds were not mechanically tested to determine the effect of this porosity on mechanical properties. It may be possible to reduce the amount of porosity by determining the minimum level of rare earths required to prevent hydrogen cracking. Further testing is indicated to verify the results and to optimize the rare-earth addition.

TABLE 6. SUBMERGED ARC WELDING TEST DATA

Weld Designation	Test No.	Main Filler Wire	Rare Earth Filler Wire	Rare Earth Addition		Volts	Travel (mm/sec)	Flux	No. of Passes	Flux Condition
				Wt. %	Wt. %					
V-10	1	L-140	FF8-115-4	1.00	400	30	394	0091	12	Dry
V-11	2	L-140	FF8-115-4	0.50	400	30	394	0091	12	Damp
V-12	3	L-140	FF8-115-4	0.50	400	30	394	0091	12	Very wet
V-13	4	L-140	--	0.00	400	30	394	0091	13	Very wet

Preheat and interpass temperatures were maintained at 250° F.

Flux designated dry was baked at 750° F for 1 hour.

Flux designated damp was exposed to 100% humidity at 100° F for 1 hour.

Flux designated very wet was exposed to 100% humidity at 100° F for 24 hours.

The rare earth addition to the weld metal assumes a 100% recovery rate.

Base plate material was HY-130.

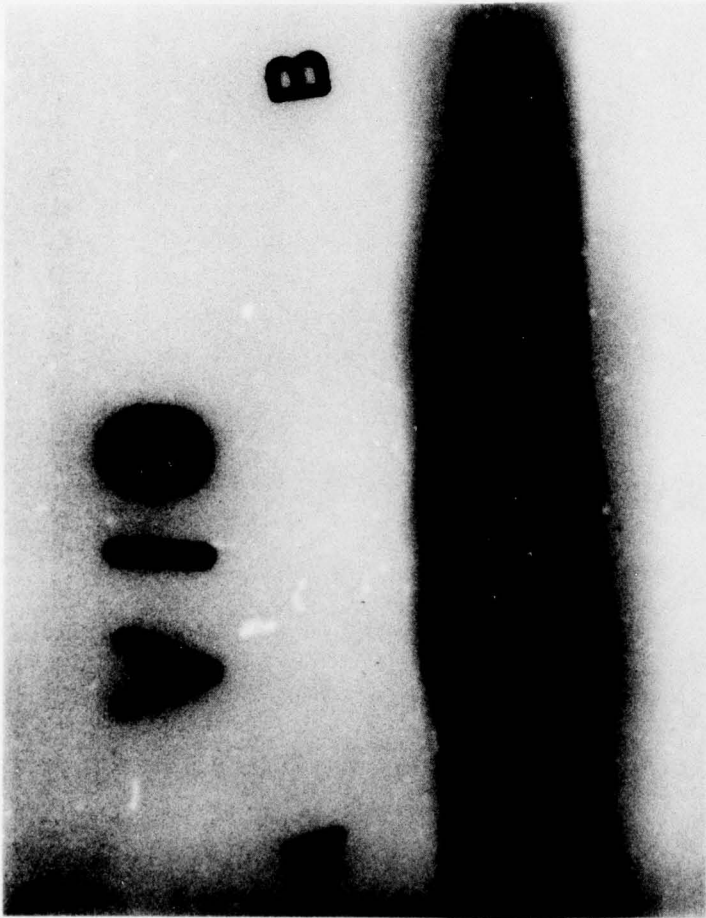


FIGURE 14. RADIOGRAPH OF WELD V-10
1.0 percent Rare-Earth Addition
Dry Flux

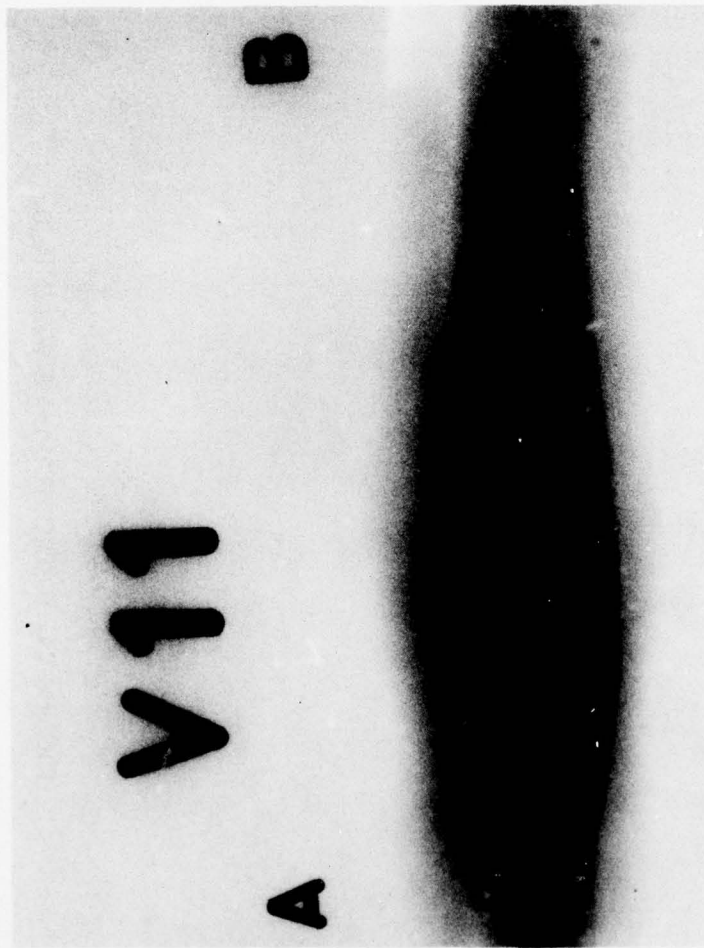


FIGURE 15. RADIOGRAPH OF WELD V-11

0.5 percent Rare-Earth Addition
Damp Flux



FIGURE 16. RADIOGRAPH OF WELD V-12

0.5 percent Rare-Earth Addition
Very Wet Flux



FIGURE 17. RADIOGRAPH OF WELD V-13
0.0 percent Rare-Earth Addition
Very Wet Flux

Hydrogen gettering tests were conducted by melting buttons of two of the weld metals under hydrogen-rich argon. These tests were performed identically to previous gettering tests. The results are shown in Table 7. The results are very interesting in that a 0.5 percent rare-earth weld metal appears capable of gettering more hydrogen than a 1.0 percent rare-earth weld metal.

CONCLUSIONS AND RECOMMENDATIONS

Much of the early work on this program dealt with finding a method for adding rare-earth compounds to the weld pool. Attempts to incorporate the rare earth in the *high-strength filler wire met with limited success due to wire-forming problems*. The most successful method found for adding rare-earth materials during welding was via a rare-earth cored wire analogous to conventional flux-cored wire. The use of a rare-earth cored wire offers great flexibility through changes in core composition or sheath composition. It was found that these cored wires had to be cold drawn without lubricants to avoid oxidizing the rare-earth compounds in the core during postdrawing heat treatment.

Hydrogen-gettering tests have shown that the rare-earth nickel-cored wire is a more effective getter than the rare-earth silicon-cored wire. Also, the addition of iron powder to the core of the rare-earth nickel wire slightly decreased its gettering ability. The use of different high-strength filler wires, AX-140 or L-140, did not seem to alter the performance of any of the rare-earth wires.

Problems were encountered with the use of the rare-earth wires in gas metal-arc welding (GMAW). The rare-earth cored wires were added to the weld pool as a cold wire ahead of the main filler. When argon-oxygen shielding gases were used, the rare earth was oxidized and none was retained to getter hydrogen. In pure argon shielding, the rare-earth addition caused very unstable arc operation resulting in poor welds and, in some cases, cracking was observed. Welds produced under pure argon showed no ability to retain residual rare earth for postgettering of hydrogen. Subsequent button melting tests strongly indicated that following initial melting, the rare-earth compounds were incapable of gettering hydrogen. The failure to detect any residual rare earth in the microprobe examination of weld metal suggested that the rare-earth addition

TABLE 7. HYDROGEN GETTERING TESTS WITH SUBMERGED ARC WELD METAL

Specimen No.	Sample Material		Rare Earth, Percent	Percent H ₂ in Argon	Length of H ₂ Gas Column Evolved (mm)	H ₂ Evolved Per Unit Weight ml/g
	Total of 10 Gram Wt.	Sample Origin				
108	L-140	Filler wires	0.00	0.5	8	0.011
109	L-140, R.E.-Ni (FF8-115-3)	Filler wires	0.40	0.5	1	0.001
110	L-140, R.E.-Ni (FF8-115-3)	Weld V-10	1.00	0.5	13	0.018
111	L-140, R.E.-Ni (FF8-115-3)	Weld V-11	0.50	0.5	3	0.004
112	L-140, R.E.-Ni (FF8-115-3)	Weld V-10	1.00	0.5	8	0.011
113	L-140, R.E.-Ni (FF8-115-3)	Weld V-11	0.50	0.5	3	0.004
114	L-140,	Filler wires	0.00	0.5	8	0.011
115	L-140, R.E.-Ni (FF8-115-3)	Weld V-10	1.00	0.5	8	0.011

scavenged oxygen provided by the weld metal and filler metal and then floated out of the pool as a slag. Further tests in which aluminium was added to the button did not demonstrate that the rare earth could be protected from oxidation. It was also shown that aluminum itself does not affect hydrogen absorption or release.

Rare-earth additions can be made as a cold-wire addition to the submerged-arc welding process. Tests conducted to duplicate fabrication situations demonstrated that a rare-earth addition can tie up diffusible hydrogen and prevent delayed hydrogen cracking. In one case, a 0.5-percent rare-earth addition was used in conjunction with a wet (held at 100 percent humidity and 100 F for 24 hours) flux and no hydrogen cracking was observed. When the same test was duplicated without a rare-earth addition, transverse hydrogen cracking occurred. This method could have many applications where materials susceptible to hydrogen cracking are welded by the submerged-arc process, especially in situations where the flux is prone to moisture pickup and bakeout procedures are costly and difficult to enforce.

Further investigation of the rare earth - submerged-arc application is necessary to determine optimum levels of rare-earth addition and the resulting mechanical properties. The ability to protect the rare earth in a flux environment suggests that rare earths might be added to the coating of basic covered electrodes of the low hydrogen variety. This might necessitate lowering the curing temperature for these electrodes, but the end product could be a much greater tolerance for moisture absorption in the production welding environment. Another area of application of rare-earth cored wires is in electroslag welding. There is some speculation that microfissuring in electroslag welds of lower strength materials may be caused by hydrogen. It may also be possible to utilize rare earths in cored wires for flux-cored arc welding (FCAW) of high-strength materials.

In conclusion, further experimental work is necessary to determine a practical method for incorporating rare-earth materials in GMAW welds. This work should include a detailed investigation of welding parameters including changes in slope, inductance, polarity, shielding gases, and wire orientations. The use of the plasma-MIG process could have potential advantages from the standpoint of arc stability and rare-earth protection from oxidation. Further studies are necessary to define more clearly the effect of rare earths on mechanical properties and, if deleterious, to ascertain the cause and solution.

The great potential of rare-earth materials to mitigate the universal hydrogen embrittlement problem strongly recommends that further studies be conducted with the end goal of industrial utilization.

REFERENCES

1. D. G. Howden and D. R. Milner, "Hydrogen Absorption in Arc Welding", British Welding Journal, June, 1963, p 304.
2. C. S. Kortovich, "Inhibition of Hydrogen Embrittlement in High-Strength Steel", prepared for Office of Naval Research under Contract N00014-74-C-0365, February, 1977.
3. Reference Annual Report, ONR Contract No. N00014-74-C-0407 (NR031-770), July 31, 1975.
4. Reference Annual Report, ONR Contract No. N00014-74-C-0407 (NR031-770), July 31, 1976.
5. Reference Annual Report, ONR Contract No. N00014-74-C-0407 (NR031-770), July 31, 1977.
6. C. E. Jackson, "Control of Welding Performance by Selected Technique Parameters", IIW Document XII K-85-77, 1977.
7. C. E. Jackson, "Submerged-Arc Welding of HY-130, A Status Report", 1977, The Ohio State University.